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Final Technical Report

Reaction Kinetics in Flames

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with the collaboration of

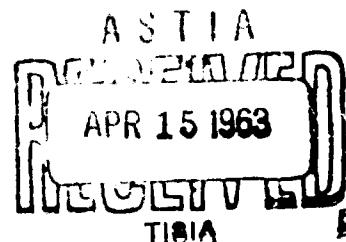
R. Burke and J. D'Olieslager

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ABSTRACTS

FIRST SECTION

Flame propagation velocities and temperatures have been measured in propylene-oxygen mixtures at different mixture strengths and varying dilutions with nitrogen. An activation energy of 40 kcal and a mean molecular weight of chain carriers can be derived from these measurements. The reaction mechanism is discussed, it points out the stability of the $C_3H_5^{\cdot}$ radical.

SECOND SECTION

A comparative study is made of flames propagating in mixtures of nitrous oxide and CH_4 , C_2H_6 , C_3H_8 , $n-C_4H_{10}$, $i-C_4H_{10}$, $C(CH_3)_4$, C_2H_4 , C_2H_2 , C_3H_6 .

The overall activation energy of the branching process has been calculated together with the mean molecular weight of the free radicals which are responsible for the propagation of the chain reaction. A reaction mechanism is proposed based on the formation of alkoxy radicals according to $R^{\cdot} + N_2O \rightarrow RO^{\cdot} + N_2$, followed by $RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$.

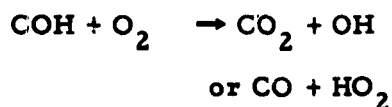
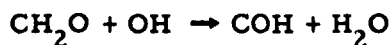
INTRODUCTION

It is often assumed that the high temperature in the flame renders the kinetical study of the chemical processes in the flame very intricate. This might be partly true but on the other side the absence of wall effects makes that the reaction zone of a flame constitutes in some respect an ideal reactor if the temperature level would not be so high.

Indeed in the flame the degradation of the initial molecules reaches necessarily a very high degree of division : small and not elaborated radicals are formed starting from even very complicated structure in the large molecules of the different fuels. It might be at first sight a reasonable attitude to deny any signification to reaction kinetics in such extreme conditions. However in the sequence of chemical processes leading to the ultimate degradation it might also be reasonable to look after that one single process which is the rate determining step and which imposes its kinetics on the overall process of oxidation. As a rule when some organic compound reacts with oxygen the mechanism is a chain reaction and some intermediate products are found : as an example we might consider the case of methane



The formaldehyde which is formed does not accumulate but it is oxidized in turn in a secondary chain



It is unimportant to know if OH or HO₂ is produced in the last reaction since they will more or less behave in a similar manner to continue the chains. The attack of CH₂O by the OH radical is far more rapid than the attack of CH₄. This is quite general : all intermediates in any oxidation reaction present somewhere in their structure a markedly weakened bond which explains their enhanced reactivity towards the action of the free radicals.

Therefore the first attack of the fuel molecule by a free radical is really the rate determining step which will impose its kinetics on the overall reaction.

However another process will also play an important role in the sequence of reactions taking place in the flame reaction zone; namely the branching process which takes care of the maintenance of the critical concentration of free radicals in the flame front. Both processes will combine in the overall reaction rate U :

$$U = k \frac{(R)}{p} \alpha$$

k is a reaction constant; $\frac{(R)}{p}$ is the relative partial pressure of free radicals, and α is the probability of chain continuation.

$\frac{(R)}{p}$ stationary value will depend on the temperature by the exponential $e^{-E_r'/RT}$ (E_r' = activation energy of the branching process) while α will vary according to $e^{-E_p'/RT}$ (E_p' = overall activation energy of the propagation process).

As it is now definitely accepted the burning velocity V_o is proportional to the square root of U :

$$V_o \approx K \sqrt{U}$$

On the basis of these very general principles quite a series of flames have been studied in our laboratory in the past (1) (2) (3) (4) (5), and a very coherent view of the problem of reaction kinetics in flames has been

reached. Whilst our earlier work concerned the study of widely different fuels and oxidizers, our recent work concerned rather the influence of the hydrocarbon structure on the flame properties in hydrocarbon/oxygen mixtures, and in hydrocarbon/nitrous oxide flames. The most recent results will be described in this report.

SECTION ONE

KINETICS OF THE PROPYLENE - OXYGEN FLAME REACTION (*)

with collaboration of R. BURKE and F. DEWAELE

INTRODUCTION

The influence of bond energy and molecular structure on the flame propagation in some hydrocarbon-oxygen mixtures has been shown in a previous report (5). A double effect has been found by comparing the flame propagating in mixtures of oxygen and one of the hydrocarbons CH_4 , C_2H_6 , $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$, $\text{neo-C}_5\text{H}_{12}$ and C_6H_6 :

- A first observation concerns the apparent activation energy, which can be deduced in the usual way from measurements of burning velocities and flame temperatures at different ratios fuel to oxidant and different degrees of dilution with nitrogen.
- Furthermore from determinations of flame front thickness in the same varying conditions, it has been pointed out that the mean molecular weight of the chain carriers depends on the nature of the fuel.

These observations are summarized in table 1.

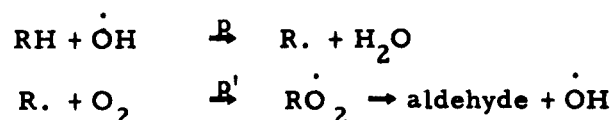
(*) The matter treated in this section has been presented for publication in "Combustion and Flame"; it will be included in one of the next issues.

TABLE 1

Hydrocarbon	activation energy E Kcal/mole	weakest C-H bond Kcal/mole	mean molecu- lar weight M	steric fac- tors ratio f
CH ₄	38 to 41	103	17	-
C ₆ H ₆	40	102	17	-
C ₂ H ₆	39	98	18	-
(CH ₃) ₄ C	38	99	28	11
n-C ₄ H ₁₀	33	94	23	8
iso-C ₄ H ₁₀	31	92	24	9

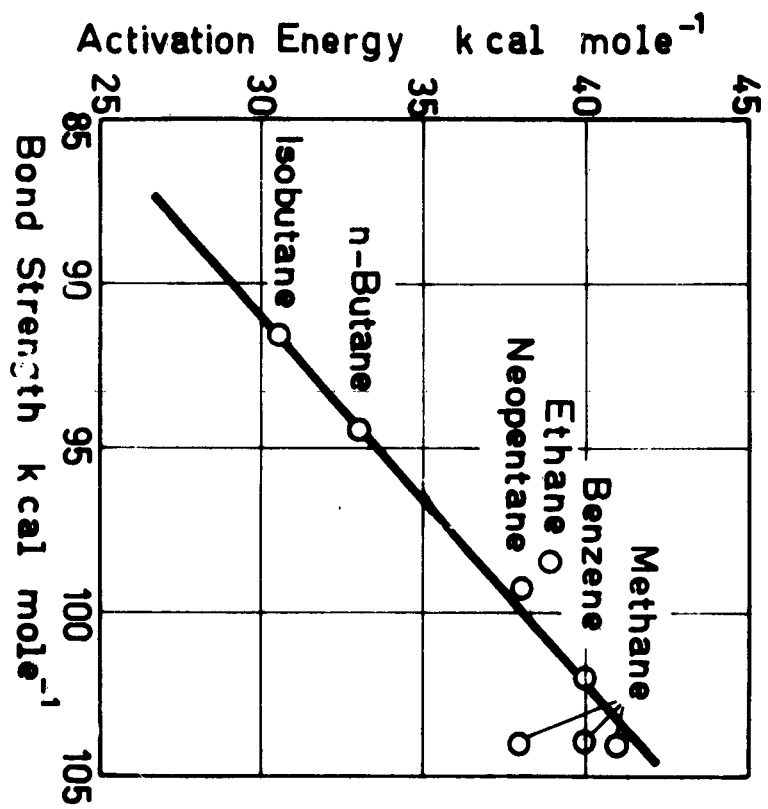
All measurements were made on stoichiometry and the slightly lean side of stoichiometry.

The data in the last column represent a rough estimation of the ratio of the steric factors $f_p/f_{p'}$, corresponding to the following reactions :



The data show that for n-butane, isobutane and neopentane the collision efficiency of reaction p' is about one-tenth that of reaction p. The lower steric factor for propagation step p' finds its explanation in the fact that a large alkyl radical must have a more specific spacial orientation to undergo an addition reaction with oxygen, whereas the orientation for an effective collision between a small reacting radical, such as OH, with a hydrocarbon is not critical.

A graph showing the relation between the weakest C-H bond energy in the hydrocarbon and the activation energy E is given in figure 1.



It has been shown in previous papers (6) (7) that the overall activation energy obtained from burning velocities at various flame temperatures mainly consists of the activation energy of the branching process (E_x), combined with the activation energies of the chain propagation steps (E_p and $E_{p'}$).

Since the latter could only differ by a few kcal when the hydrocarbon is changed, it follows that the branching process occurs more easily when it implies a fragment obtained by the abstraction of a more weakly bound hydrogen. Both effects (chain propagation and chain branching) contribute however to the reduction of the overall activation energy E .

It seemed therefore interesting to investigate the behaviour of a hydrocarbon with an abnormally low C-H bond energy. The obvious substance was propyne $\text{CH}_3\text{-CH=CH}_2$, where the bond energy of the paraffinic hydrogen only has a value of 77 kcal (8). Still it is well known that some resonance stabilisation reduces markedly the reactivity of the allyl radical $\text{CH}_2=\text{CH-}\dot{\text{C}}\text{H}_2$.

For these reasons it was difficult to foresee if propylene would find its place in the series represented on figure 1, in which case the apparent activation energy could be only 20 kcal, a remarkable low value, comparable to the activation energy found in the hydrogen-oxygen flames (9).

I. EXPERIMENTAL RESULTS

The experimental methods have been described in an earlier work and have not been changed since; they include : the measurement of the burning velocity on the schlieren image, the determination of the flame temperature and the estimation of the thickness of the flame reaction zone (10). Only measurements on unpreheated mixtures have been made. The gases were commercial grade, purity at least 99 %. All experimental results are presented in Table 2 where the following symbols are used :

R : ratio fuel to the sum of fuel plus oxygen

$$R = (C_3H_6)/(C_3H_6 + O_2)$$

% N₂ : percentage of inert nitrogen diluent

T_f^{°K} : temperature of flame as measured by the sodium line reversal method (°Kelvin)

T_m^{°K} : mean temperature of flame front (°Kelvin)

$$T_m = T_o + 0.74 (T_f - T_o) \quad (\text{see ref. 6})$$

V_o : burning velocity (cm/sec)

s : distance between visual and schlieren image (cm x 10²)

The overall activation energies are derived from the plots of :

$$\log V_o + 1/2 \log T_m - 1/2 \log Y : \text{cst} - E \log e / 2 RT_m$$

$$Y = (100 - \% N_2) / 100 \quad (\text{see ref. 5})$$

A mean activation energy E of about 40 kcal is obtained.

When the V_o/√T_m values are plotted versus 1/s, according to the relation

$$\frac{V_o}{\sqrt{T_m}} = \frac{1.8 \times 10^{-1}}{\sqrt{M}} \quad \frac{1}{s}$$

the mean molecular weight M of the chain carriers is obtained from the

slope of the straight line (10). A value of 32 is obtained which is much higher than 17, the molecular weight of the OH radical but not yet equal to 41, the molecular weight of the C_3H_5 allyl radical.

TABLE 2

R	N ₂ %	T _f °K	T _m °K	V _o cm/sec	s cm x 10 ²
0.1818	77.5	2163	1677	35	2.54
	75	2275	1760	48	2.22
	72.5	2370	1830	62	1.99
	70	2450	1889	77	1.76
	67.5	2516	1938	91	1.55
	65	2563	1973	108	1.39
	62.5	2598	1998	121	1.23
	60	2622	2016	135	1.14
0.16	77.5	2107	1635	34	2.80
	75	2214	1714	51	2.34
	72.5	2307	1783	63	2.09
	70	2383	1839	76	1.86
	67.5	1450	1889	91	1.65
	65	2504	1929	106	1.45
	62.5	2548	1961	115	1.32
	60	2581	1986	127	1.20
0.14	57.5	2607	2005	136	1.10
	75	2157	1672	46	2.57
	72.5	2251	1742	59	2.13
	70	2330	1800	72	1.92
	67.5	2401	1852	85	1.72
	65	2455	1892	97	1.54
	62.5	2496	1923	110	1.37

TABLE 2 (continued)

R	N ₂ %	T _f °K	T _m °K	V _o cm/sec	s cm x 10 ²
0.12	60	2532	1950	117	1.23
	57.5	2560	1970	127	1.12
	55	2581	1986	138	1.03
	72.5	2110	1637	43	2.55
	70	2195	1700	58	2.39
	67.5	2272	1757	68	2.00
	65	2337	1805	80	1.80
	62.5	2396	1849	94	1.59
	60	2448	1888	106	1.40
	57.5	2491	1919	116	1.28
	55	2528	1947	122	1.12
	52.5	2557	1968	143	0.99
	67.5	2157	1672	52	2.01
	65	2213	1713	66	1.88
	62.5	2265	1752	72	1.71
0.10	60	2313	1787	87	1.56
	57.5	2357	1820	95	1.41
	55	2398	1851	106	1.29
	52.5	2435	1878	116	1.18
	50	2468	1902	126	1.09
	47.5	2496	1923	137	1.03

II. DISCUSSION OF RESULTS

The value of the overall activation energy (40 kcal) does not fit with the results presented in figure 1, since the weakest C-H bond in propylene is only 77 kcal, and by extrapolation a value of only 20 kcal would be obtained. Furthermore the observed molecular weight of 32 is even larger than 28, obtained with mixtures of oxygen and neopentane, a still heavier hydrocarbon (see table 1). The only possible explanation has to be found in the resonance stabilisation of the C_3H_5 allyl radical which renders it much less reactive. This has two consequences which are discussed now.

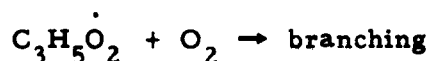
1. The reactivity of the C_3H_5 radical and the branching reaction.

As shown in a previous paper (11), the overall activation energy E has an intermediate value between E_r (activation energy of the chain branching process) and $E_r + E_p - E_{p'}$, or $E_r - E_p + E_{p'}$, (E_p and $E_{p'}$ are the activation energies of the alternating chain propagation steps). The choice between the two latter possibilities is not arbitrary. If the branching reaction occurs between the oxygen molecule and the C_3H_5 radical :



the limit value of E is $E_r - E_p + E_{p'}$.

If however the branching reaction occurs between the oxygen molecule and some radical which was in turn formed by the reaction of the initial C_3H_5 radical with oxygen :



the limit value of E becomes $E_r + E_p - E_{p'}$.

To explain the experimental overall activation energy E we must

resort to these combinations of the three true activation energies of the elementary processes : E_r , E_p and $E_{p'}$. Their values for propylene, related to the other hydrocarbons, can be estimated as follows :

- E_{r_1} for the reactions $\dot{C}_3H_5 + O_2 \rightarrow$ branching

probably is very large. This is not surprising as the resonance stabilisation of the allyl radical reduces its reactivity.

- E_{r_2} for the reaction : $C_3H_5O_2\cdot + O_2 \rightarrow$ branching

cannot be so large as E_{r_1} because of the smaller stabilisation of the allyl peroxy radical, the molecule being not symmetrical. Moreover the reaction of oxygen with the allyl peroxy radical will be more exotherm than with the allyl radical. This again tends to lower the activation energy.

- E_p of reaction : $C_3H_6 + \dot{O}H \rightarrow \dot{C}_3H_5 + H_2O$

must be smaller than for other hydrocarbons, as this reaction involves the attack of a very weak C-H bond (Polanyi and Semenov relation between activation energy and enthalpy change).

An estimation for E_p is 0.5 kcal, the same value as for reaction $H_2CO + \dot{O}H \rightarrow H_2\dot{O} + HCO$, which has the same enthalpy change (12).

- $E_{p'}$ of reaction : $\dot{C}_3H_5 + O_2 \rightarrow C_3H_5\dot{O}_2 \rightarrow$ intermediate + $\dot{O}H$ is higher as compared to other hydrocarbons, since this reaction again involves the allyl radical, it could be as high as 6 kcal.

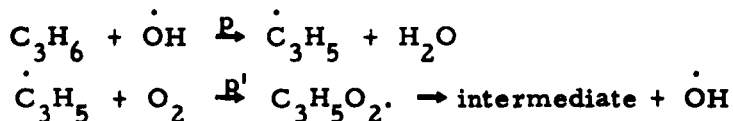
A strong argument for a high value is the use of propylene to inhibit low temperature chain reactions. This inhibition is explained by the unusual stability of the allyl radical (13).

For the first branching model ($\dot{C}_3H_5 + O_2$) the experimental activation energy $E \approx E_{r_1} - E_p + E_{p'} = 40$ kcal leads to a value of ~ 35 kcal for E_{r_1} , whilst for the second model ($C_3H_5O_2\cdot + O_2$) the activation energy $E \approx E_{r_2} + E_p - E_{p'} = 40$ kcal leads to a value of 45 kcal for E_{r_2} .

It is very seductive to assume the second model, because of its analogy with the proposed mechanisms for the other hydrocarbons (5) (11), but we cannot decide which of both branching mechanisms is to be accepted.

2. Mean life periods of the chain carriers.

If we suppose that the alternating chain propagation steps are :



the mean molecular weight is given by :

$$M = (M_{\text{OH}} \tau_{\text{OH}} + M_{\text{C}_3\text{H}_5} \tau_{\text{C}_3\text{H}_5}) / \tau$$

where the mean life periods of the radicals are represented by

$$\tau_{\text{OH}} \text{ and } \tau_{\text{C}_3\text{H}_5} \quad (\tau = \tau_{\text{OH}} + \tau_{\text{C}_3\text{H}_5}).$$

Since $M = 32$, we obtain $\tau_{\text{C}_3\text{H}_5} / \tau_{\text{OH}} = 1.66$

It has been shown previously (1) that :

$$\frac{\tau_{\text{C}_3\text{H}_5}}{\tau_{\text{OH}}} = \frac{f_p (\text{C}_3\text{H}_6) e^{-E_p/RT_m}}{f_{p'} (\text{O}_2) e^{-E_{p'}/RT_m}}$$

In the previous section we obtained an approximative estimation for E_p and $E_{p'}$:

$$\begin{aligned} E_p \text{ (for } \text{C}_3\text{H}_6 + \text{OH}) &\approx 0.5 \text{ kcal} \\ E_{p'} \text{ (for } \text{C}_3\text{H}_5 + \text{O}_2) &\approx 6 \text{ kcal} \end{aligned}$$

In the mean range of mixture compositions and of T_m values we may write :

-5500/1825

$$\frac{\gamma_{C_3H_5}}{\gamma_{OH}} = 1.66 \frac{f_p}{f_{p'}} \frac{0.14}{0.86} e$$

and from there $f_p/f_{p'} \approx 0.5$

This means that the collision efficiency of reaction p is about one half that of reaction p'. Here again there is a marked difference with the saturated hydrocarbons, where the collision efficiency of reaction p' is the lower. That the spacial orientation for an allyl radical to undergo an addition reaction with oxygen is less critical than for the other alkyl radicals is due to the resonance stabilisation of the allyl radical. In this radical the free electron is not bound at a specific place, the $(CH_2 \text{ --- } CH \text{ --- } CH_2) \cdot$ allyl radical can be attacked by the oxygen molecule at either carbon. Any contribution of a heavier radical than OH (such as a peroxy radical) to the mean molecular weight of 32 of chain carriers would necessarily lower the value of $\gamma_{C_3H_5}/\gamma_{OH}$, and as a result also lower the ratio $f_p/f_{p'}$.

Evidently both these latter ratios depend slightly on the temperature and on the mixture composition, and the estimation here above is only approximately valid in the mean range investigated here.

In more extreme conditions such as much leaner or richer mixtures and lower or higher dilution with N_2 , the changes of the relative life periods would be much more important and some variation in the mean molecular weight of the chain carriers ought to be observed. Some work in this direction is now being undertaken for a series of different hydrocarbons.

CONCLUSIONS

The properties of propylene-oxygen flammable mixtures differ markedly from the behaviour of saturated hydrocarbons. An explanation is to be found in the resonance stabilisation of the C_3H_5 radical. This corresponds to the higher activation energies of the reactions involving the C_3H_5 radical. Obviously a similar study should be undertaken concerning the properties of the toluene - oxygen mixtures where a kindred situation is to be expected.

This will make the object of a future investigation.

SECTION TWO

KINETICAL STUDY OF HYDROCARBON-NITROUS OXIDE FLAMES (*)

with the collaboration of J. D'OLIESLAGER

INTRODUCTION

In an earlier publication a study has been made of the flames propagating in mixtures of nitrous oxide with acetylene (1) (9) and with methane (4). Some results concerning the latter case have not yet been published and are included in this report where a comparative study of hydrocarbon flames supported by nitrous oxide is extended to the following hydrocarbons : ethane, propane, n-butane, isobutane, neopentane, ethylene and propylene. This work has been undertaken as the continuation of a general kinetical study of the flames which propagate in hydrocarbons.

Very recently some interesting correlations have been pointed out between the structure of the hydrocarbon molecule and both the mean molecular weight of the chain carriers and the overall activation energy of the branching process (5).

When nitrous oxide replaces the oxygen in flammable mixtures, a very important decrease of burning velocity is observed, even when comparing two mixtures with the same flame temperature. As it will be shown in the discussion at the end of this part, the observed decrease results from an increase in the overall activation energy and also, in some cases, from a marked increase of the mean molecular weight of the free radicals which are responsible for the propagation of the chain reaction.

(*) The research reported in this section will be presented in the future, when completed, for publication, probably in the periodical "Combustion and Flame".

I. EXPERIMENTAL RESULTS

All measurements were made on stoichiometric mixtures at different degrees of dilution with nitrogen. The experimental results are given in table 3, where the following symbols are used :

% N₂ : degree of dilution with N₂

V_o : burning velocity (cm/sec)

T_f : final temperature of the flame (°K)

T_m : mean temperature of the flame reaction zone, as estimated from the approximation (6)

$$T_m = T_o + 0,74 (T_f - T_o)$$

T_o : temperature of the fresh gases

s : distance between the schlieren and the visual image of the flame.

The mean molecular weight M of the chain carriers is given in the last column, they have been calculated according to the following equation (10) :

$$\frac{V_o}{\sqrt{T_m}} = \frac{1.8 \times 10^{-1}}{\sqrt{M}} \frac{1}{s}$$

The overall activation energy of the branching process has been obtained for each series related to a given hydrocarbon from a plot of

$$\log V_o + 1/2 \log T_m - 1/2 \log Y$$

against the reciprocal of T_m (11); Y represents the ratio

$$Y = \frac{100 - \% N_2}{100}$$

The obtained activation energies are reported in Table 3 ahead of series of experiments.

TABLE 3

% N ₂	V _o cm/sec	T _f °K	T _m °K	s cm x 10 ²	M
CH ₄ + N ₂ O E = 56.5 kcal					
25.0	69.0	2675	2056	2.38	31
27.0	-	2665	2048	-	31
30.0	58.0	2620	2015	2.80	31
35.0	50.0	2580	1985	3.08	31
38.3	-	2540	1956	-	31
40.0	41.0	2520	1941	3.50	31
42.5	-	2470	1904	-	31
45.0	31.0	2430	1874	4.18	31
50.0	25.0	2335	1804	-	31
C ₂ H ₆ + N ₂ O E = 52.0 Kcal					
30	65.5	2671	2051	2.48	30.8
35	57.9	2611	2012	2.76	30.8
40	50.2	2564	1973	3.16	30.8
45	46.4	2503	1928	3.73	30.8
50	35.0	2436	1879	4.83	30.8
55	27.0	2364	1826	-	32.7
60	16.4	2290	1771	6.40	38.2
C ₃ H ₈ + N ₂ O E = 66.0 Kcal					
40	47.2	2611	2011	2.88	33.8
45	39.3	2565	1976	3.50	35.9
50	31.0	2510	1934	4.11	39.6
55	24.2	2448	1885	4.96	46.7
60	17.3	2376	1829	6.54	49.1
65	12.5	2244	1741	9.70	50.0

TABLE 3 (continued)

% N ₂	V _o cm/sec	T _f °K	T _m °K	s cm x 10 ²	M
n-C ₄ H ₁₀ + N ₂ O E = 61.6 kcal					
35	52.0	2635	2026	3.37	21.4
40	46.4	2595	1998	3.52	26.1
45	37.8	2549	1962	4.20	28.1
50	29.2	2483	1914	5.31	30.4
55	20.2	2373	1832	6.67	33.5
60	10.8	2143	1662	11.89	35.6
iso-C ₄ H ₁₀ + N ₂ O E = 59.5 kcal					
40	44.6	2573	1979	3.28	32.5
45	38.4	2540	1955	3.71	33.3
50	33.3	2500	1926	4.10	38.3
55	25.2	2436	1877	4.45	48.6
60	19.6	2360	1822	4.98	64.2
neo-C ₅ H ₁₂ + N ₂ O E = 60.6 kcal					
35	51.9	2643	2030	3.01	26.4
40	46.3	2584	1996	3.53	28.7
45	42.2	2672	1959	4.50	31.8
50	30.6	2483	1914	4.96	33.7
55	22.8	2424	1860	5.49	36.3
60	15.3	2268	1755	8.31	38.2

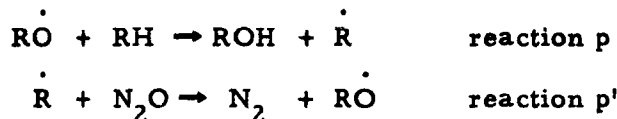
TABLE 3 (continued)

% N ₂	V _o cm/sec	T _f °K	T _m °K	s cm x 10 ²	M
C ₂ H ₄ + N ₂ O E = 53.1 kcal					
40	55.0	2627	2018	3.05	23.8
45	47.1	2594	1987	3.13	31.3
50	38.3	2525	1942	3.44	38.2
55	30.7	2436	1888	3.88	43.0
60	22.5	2355	1822	4.75	43.0
C ₂ H ₂ + N ₂ O E = 54.0 kcal					
20 to 35*					17
40	81.5	2740	2102	2.22	22.2
45	69.5	2690	2069	2.39	25.0
50	56.6	2643	2030	2.94	26.9
55	44.0	2576	1971	3.38	27.7
60	30.3	2416	1874	5.25	31.8
65	20.2	2268	1749	5.64	41.0
C ₃ H ₆ + N ₂ O E = 63.1 kcal					
35	52.1	2650	2037	2.54	40.0
40	45.4	2611	2009	2.97	42.3
45	40.4	2576	1979	3.22	45.6
50	33.6	2534	1941	3.47	51.2
55	24.0	2432	1893	4.84	57.0
60	19.5	2376	1829	5.34	57.0
65	10/0	2138	1658	9.07	57.0

* From reference (9)

II. INTERPRETATION OF EXPERIMENTAL DATA

An almost obvious mechanism for the chain reaction accounting for the oxidation of hydrocarbons by nitrous oxide seems to be as follows :



Evidently the alcohol formed as an intermediate product will simultaneously be further oxidized by a parallel chain mechanism. Because of the fact however that all C-H Bonds in the alcohol will never be enhanced (they will rather be weakened in the vicinity of the hydroxyl group), it seems safe to assume that this parallel chain will have no or little influence on the main primary chain proposed here above. The proposed mechanism accounts for the observed value of 31 as representing the mean molecular weight of the chain carriers in the $\text{CH}_4 - \text{N}_2\text{O}$ mixtures : indeed reaction p has a larger activation energy (E_p) than reaction p' ($E_{p'}$) and the apparent molecular weight (7) will be near to the value of 31

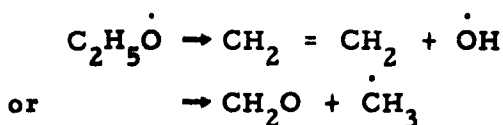
$$M = M_x \frac{\tau_x}{\tau} + M_y \frac{\tau_y}{\tau}$$

where $X = \dot{\text{R}}$ and $Y = \dot{\text{RO}}$ and, therefore, $\tau_x \ll \tau_y$.

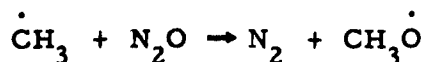
Nevertheless when the hydrocarbon molecule has a more complex structure than methane, a further decomposition of the alkoxy radical can occur which explains the values of M obtained with the other hydrocarbons and which will be now discussed :

1. C_2H_6

The further decomposition of the alkoxy radical $\text{C}_2\text{H}_5\dot{\text{O}}$ could be



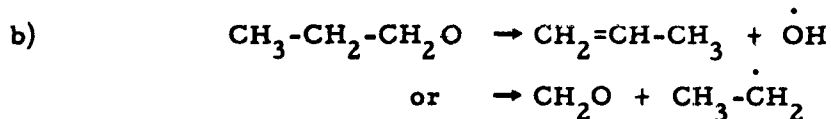
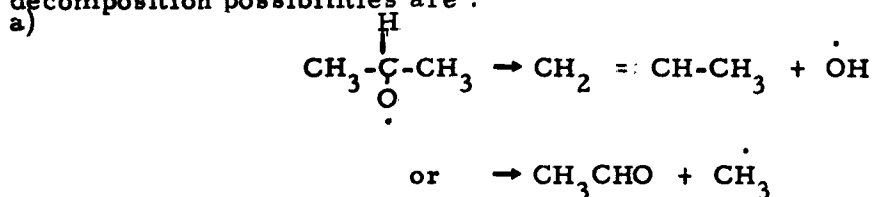
followed by



Therefore, if decomposition occurs, the apparent molecular weight of the Y radical would be that of one (or both) of the radicals $\text{CH}_3\dot{\text{O}}$ and $\dot{\text{O}}\text{H}$: this explains why the largest obtained value is only 38.2 instead of 45 ($\text{C}_2\text{H}_5\text{O}$).

2. C_3H_8

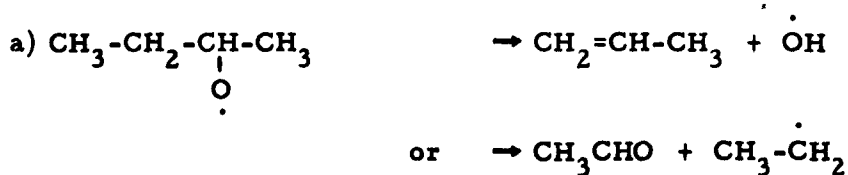
Two possibilities exist for the $\text{C}_3\text{H}_7\text{O}$ radical, depending on the previous abstraction of a primary or secondary hydrogen. The decomposition possibilities are :

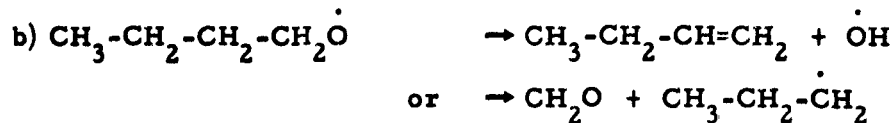


The $\text{CH}_3 - \dot{\text{C}}\text{H}_2$ radical reacts further in the same way as in the previous case.

3. $\text{n-C}_4\text{H}_{10}$

Here again two possibilities exist :

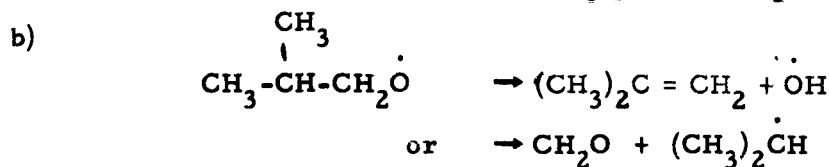
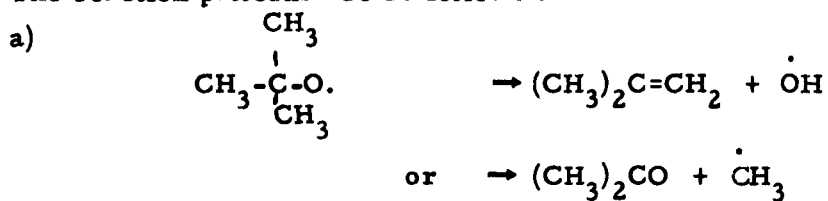




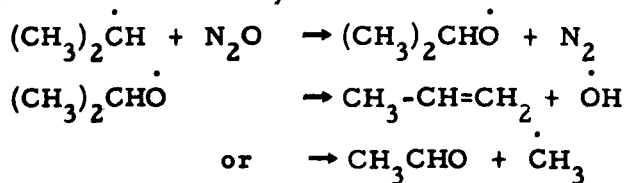
The $\text{CH}_3\text{-CH}_2\text{-}\dot{\text{C}}\text{H}_2$ radical will follow an identical reaction pattern as explained in connection with propane.

4. iso-C₄H₁₀

The reaction patterns are as follows :

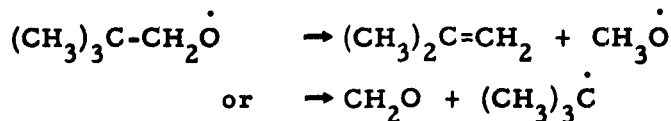


which would be followed by :



The further reactions of $(\text{CH}_3)_2\dot{\text{C}}\text{H}$ and $\dot{\text{C}}\text{H}_3$ already have been explained.

5. neo-C₅H₁₂



The latter reacts as explained in connection with iso-C₄H₁₀.

6. C₂H₄

There is only one possibility here :



7. C₂H₂

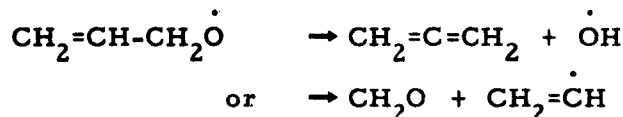
Same remark as here above



8. C₃H₆

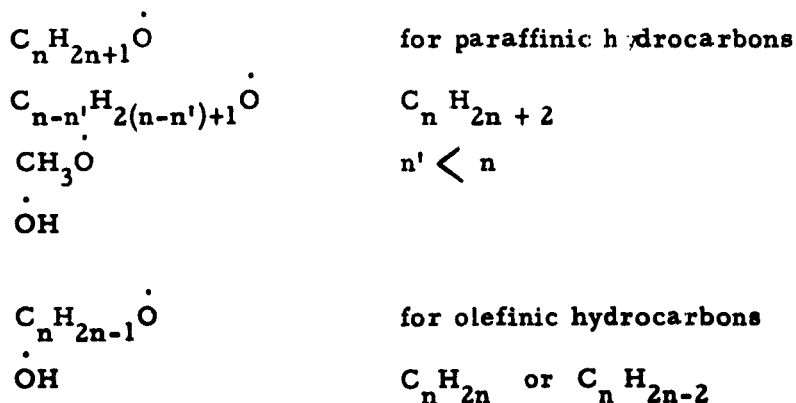
The attack of the propylene molecule occurs necessarily on the exceptionally weak C-H bond (8) of the methyl part of the molecule.

Therefore only one alkoxy radical can be considered :



The $\dot{\text{C}}\text{H}_2-\text{CH}$ radical finally gives, as explained in the case of ethylene, the OH radical.

By examination of the different elementary processes presented here above, one is brought to the conclusion that the Y radical in the hydrocarbon combustion with nitrous oxide represents one of the following radicals :



Furthermore it seems plausible that the decomposition of the initial alkoxy radical will be favoured at higher temperature and that the apparent mean molecular weights of the chain carriers will have a tendency to decrease at higher flame temperature : this corresponds to the general trend of our observations.

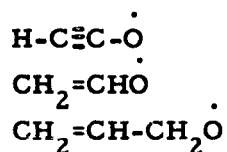
It seems however premature to draw some conclusions about the relative stability of the primary alkoxy radicals from the only results which are presented here : a more thorough study would be needed.

Nevertheless the comparison of $n\text{-C}_4\text{H}_9\dot{\text{O}}$ and $\text{iso-C}_4\text{H}_9\dot{\text{O}}$ for example leads to the conclusion that the latter, or its further decomposition product has a greater stability than the former; this results from the highest value of M in isobutane (64) as compared to the theoretical largest values of M (molecular weight of the primary alkoxy radical) and the largest values observed at the lowest flame temperatures is presented in Table 4.

TABLE 4.

hydrocarbon	theoretical largest M	observed highest M
$\cdot\text{CH}_4$	31	31
C_2H_6	45	38.2
C_3H_8	59	50
$n\text{-C}_4\text{H}_{10}$	73	35.6
$\text{iso-C}_4\text{H}_{10}$	73	64.2
$(\text{CH}_3)_4\text{C}$	87	38.2
C_2H_4	43	43
C_2H_2	41	41
C_3H_6	57	57

The highest theoretical value of M has only been observed with the unsaturated hydrocarbons at the lowest flame temperatures. This indicates a higher stability of the following radicals



The stability of the first and the second radical can be explained by the triple and the double bond. The stability of the $\text{CH}_2=\text{CH}-\text{CH}_2\text{O}$ radical can probably be compared with the extraordinary stability of the $\text{CH}_2=\text{CH}-\text{CH}_2$ (allyl) radical observed in the propylene-oxygen flame reaction. (section one).

It is quite possible that the $\text{CH}_2=\text{CH}-\text{CH}_2\text{O}$ radical is stabilized by resonance.

It will be pointed out here that larger values of M in hydrocarbon nitrous oxide flames as compared to hydrocarbon-oxygen flames lead

necessarily to a slight decrease of burning velocity because of the fact that the diffusion of the chain carriers ahead of the flame varies as the reciprocal of the square root of M (7).

However a much larger reduction of the burning velocity results from the fact that the overall activation energy in the flames sustained by nitrous oxide is much larger than in the corresponding flame burning with oxygen (Table 5).

TABLE 5

Hydrocarbon	Overall activation energy of branching with	
	N ₂ O	O ₂
CH ₄	56.5	40 (14)
C ₂ H ₆	52.0	39 (14)
C ₃ H ₈	66.0	-
n-C ₄ H ₁₀	61.6	33 (5)
iso-C ₄ H ₁₀	59.5	30.5 (5)
(CH ₃) ₄ C	60.6	38.3 (5)
C ₂ H ₄	53.1	36 (14)
C ₂ H ₂	54.0	32 (15)
C ₃ H ₆	63.1	40 (section one)

The relation between the activation energy and the strength of the weakest C-H bond, as observed with oxygen flames (5), does not seem to hold here : there is at present no indication as to the nature of the branching process in hydrocarbon-nitrous oxide flames and it would be hazardous to give some interpretation to the data given in the second column of table 5; to this problem we hope to contribute in future work.

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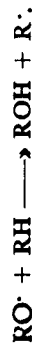
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The overall activation energy of the branching process has been calculated together with the mean molecular weight of the free radicals which are responsible for the propagation of the chain reaction. A reaction mechanism is proposed based on the formation of lakoxy radicals according to $\text{R}^\cdot + \text{N}_2\text{O}^\cdot \longrightarrow \text{RO}^\cdot + \text{N}_2$, followed by



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